CARRIER GRANULES CONTAINING LIQUID ACTIVE COMPOUNDS

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ABSTRACT
In the combating of agricultural and horticultural pests by applying to a locus from which it is desired to exclude such pests a normally liquid active compound and a normally solid active compound, the improvement which comprises applying such active compound in the form of granules comprising
a) carrier granules having a non-absorptive surface,
b) at least one liquid active compound,
c) at least one adhesive based on polyurethane as a binder, optionally mixed with a further adhesive selected from the group consisting of polyvinyl acetate, polyvinylpyrrolidone, polyvinyl alcohol, copolymers of vinyl acetate/di-n-butyl maleate, acrylic acid ester, vinyl acetate/ethylene, vinyl acetate/ethylene/vinyl chloride, vinyl acetate/acyrlic acid ester, vinyl acetate/vinyl ester and styrene/acrylic acid ester, and
d) optionally an additive.

10 Claims, No Drawings
CARRIER GRANULES CONTAINING LIQUID ACTIVE COMPOUNDS

The present invention relates to new carrier granules containing liquid active compounds (so-called "monocarrier granules"). According to the invention, active compound is preferably understood as meaning the active components of the plant protection area, such as insecticides, nematicides, acaricides, fungicides, herbicides and growth regulators.

The invention furthermore relates to a process for the preparation of the new monocarrier granules and their use for combating pests, preferably in the agricultural and horticultural field.

Numerous carrier granules are already known which contain solid or liquid biocidal active compounds on a granular carrier material (compare Bübel, "Pflanzenschutz und Schädlingsbekämpfung" (Plant Protection and Pest Control), Georg-Thieme Verlag, Stuttgart, 1977, pages 198 and 199).

Carrier granules containing liquid active compounds can be prepared, for example, by immobilizing the active components in finely divided form, if appropriate mixed with additives, on the compact or non-absorbent surface of the carrier material with the aid of various adhesives. Carrier granules containing only liquid active compounds were unable to be prepared with sufficient resistance to abrasion by this method.

Carrier granules which contain liquid biocidal active compounds can be prepared, for example, by immersing porous or absorbent carrier materials in suitable solvents containing liquid active compounds or containing solutions of liquid active compounds, in each case optionally mixed with additives. The properties of these granules, however, are not always satisfactory. Because of the low hardness of the absorbent granules, these can abrade under the stress of physical forces and thus release biocide-containing dust.

New carrier granules containing liquid active compounds have now been found which contain

a) granular carrier material having a non-absorbent surface,

b) at least one liquid active compound,

c) at least one adhesive based on polyurethane as a binder, optionally mixed with a further adhesive based on one of the following systems: polyvinyl acetate, polyvinylpyrrolidone, polyvinyl alcohol, copolymers of vinyl acetate/di-n-butyl maleate, acrylic acid esters, vinyl acetate/ethylene, vinyl acetate/ethyene/vinyl chloride, vinyl acetate/acrylic acid esters, vinyl acetate/vinyl esters, styrene/acrylic acid esters, then a mixture containing the liquid active compounds and extenders is added, the product is optionally sprayed again with an aqueous dispersion of a further adhesive based on the abovementioned systems and the granular products thus obtained are dried.

Finally, it has been found that the monocarrier granules according to the invention can be used, depending on the active compounds contained, for a variety of purposes in agriculture and horticulture.

It is to be noted as extremely surprising that the monocarrier granules according to the invention show a better activity than previously known granules in which liquid active compounds are absorbed onto porous or absorbent carrier materials in the form of a solution. It is also advantageous that the polyurethane compounds used as adhesives are easily degraded under environmental conditions and release the active compound, protecting the active compound from chemical influences up to release.

The monocarrier granules according to the invention are distinguished by a number of advantages. They can be prepared using equipment adjusted to non-absorbent carrier material for the application of carrier granules for the monocarrier granules is thus possible without complicated readjustment.

In addition, the active compounds (active components) contained in these granules are released at their place of use in the manner desired in each case. Moreover, the monocarrier granules according to the invention are products which are distinguished by an extremely high resistance to abrasion.

The products according to the invention are described in the present case as monocarrier granules, the monocarrier granule containing at least one liquid biocidally active compound optionally in the form microencapsulation.

In the monocarrier granules according to the invention, all customary carrier substances contained in granules of this type and having a non-absorbent surface can be employed as granular carrier materials having a non-absorbent surface. Calcite, dolomite and sand, such as, for example, quartz sand, are preferable.

The average particle diameter of the carrier materials can be varied within a certain range. In general, the average particle diameter is between 0.1 and 3.0 mm, preferably between 0.3 and 1 mm.

Active compound components are understood as meaning in the present case, as already mentioned above, all active compounds which can customarily be used in plant protection. These preferably include insecticides, nematicides, acaricides, fungicides, herbicides and growth regulators.

The granules according to the invention contain at least one active compound liquid at room temperature for the monocarrier granule. Active compounds liquid at room temperature are preferably phosphoric acid derivatives. Examples which may be mentioned are:

O-ethyl O-(2-isopropoxy-carbonyl-phenyl) W-isopropylaminotribonophosphate,
O,O-diethyl O-(2-isopropoxy-carbonyl-phenyl) W-isopropylaminotribonophosphate,
O,O-dimethyl O-(4-methylmercapto-3-methyl-phenyl)-thionophosphate,
O-ethyl O-(4-methylthio-phenyl) S-propyl-dithiophosphate, (O,O-diethyl-thionophosphoryl)-a-oximino-phenylacetoneitrile,
3  O,O-diethyl O-(3-chloro-4-methyl-7-coumarinyl)-thio-
phosphate,
S-[1,2-bis-(ethoxycarbonyl)-ethyl] O,O-dimethyl dithio-
phosphate.

An adhesive based on polyurethane, optionally mixed
with a further adhesive based on one of the following
systems: polyvinyl acetate, polyvinylpyrrolidone, poly-
vinyl alcohol and with copolymers of vinyl acetate/
di-n-butyl maleate, acrylic acid esters, vinyl acetate/
ethylene, vinyl acetate/ethylene/vinyl chloride, vinyl
acetate/acyrlic acid esters, vinyl acetate/vinyl esters,
styrene/acyrlic acid esters functions as a binder in the
monocarrier granules according to the invention.

Possible additives which may be present in the mono-
carrier granules according to the invention are exten-
ders, dyes and also water and organic solvents.

In this connection, possible extenders are preferably
fine-grain inorganic solids, such as ground natural min-
erals, for example kaolin, aluminas, tacle, chalk, quartz
powder, attapulgite, montmorillonite, sepiolite, zeolite,
bentonite, and in addition ground synthetic minerals
such as highly disperse silicic acids.

Inorganic pigments such as iron oxide, titanium diox-
ide, Prussian blue and organic dyes such as anthra-
dine, azo and metal phthalocyanine dyes may be men-
tioned as dyes which are suitable as additives.

Possible organic solvents are all organic solvents
which can customarily be used for the preparation of
carrier granules. Low-boiling organic solvents such as
methanol, ethanol, butanol and methylene chloride
are preferably.

The granules according to the invention consist of
granular carrier materials, on the non-absorptive sur-
facer of which there is a covering layer which, for mono-
carrier granules, contains at least one liquid active com-
pound. Polyurethane and mixtures of polyurethane and
polyvinyl acetate, polyvinylpyrrolidone, polyvinyl al-
cohol, and mixtures with copolymers of vinyl acetate/
di-n-butyl maleate, acrylic acid esters, vinyl acetate/
ethylene, vinyl acetate/ethylene/vinyl chloride, vinyl
acetate/acyrlic acid esters, vinyl acetate/vinyl esters,
and styrene/acyrlic acid esters, which may optionally
contain additives, act as binders. The components pres-
ent in the covering layer may in some cases also pene-
trate into indentations in the carrier material.

The percentages of the components contained in the
monocarrier granules according to the invention can be
varied within a relatively large range. The proportion
of granular carrier material is in general between 50 and
99.5% by weight, preferably between 60 and 92% by
weight. The proportion of liquid active compounds is
in general between 0.1 and 20% by weight, preferably
between 0.5 and 15% by weight.

The proportion of the polyurethane and mixtures of
polyurethane and polyvinyl acetate, polyvinylpyrroli-
done, polyvinyl alcohol, and mixtures with copolymers
of vinyl acetate/di-n-butyl maleate, acrylic acid esters,
viny acetate/ethylene, vinyl acetate/ethylene/vinyl
chloride, vinyl acetate/acyrlic acid esters, vinyl acetate/
viny esters, and styrene/acyrlic acid esters function-
ing as binding agents is in general between 0.1 and 4% by
weight, preferably between 0.3 and 3% by weight, 0.05 to
0.49 by weight, preferably 0.1 to 0.2 by weight, of
polyvinyl acetate, polyvinylpyrrolidone, polyvinyl
alcohol and proportions of the copolymers mentioned
above in general being apportioned per part of polyurethane. Additives are optionally present in
proportions of 1 to 40 parts by weight, preferably 2 to
30 parts by weight.

In the preparation of the monocarrier granules ac-
cording to the invention, preferably all those compo-
nents are used which have already been mentioned as
preferable in connection with the description of the
monocarrier granules according to the invention.

The polyurethane functioning as a binder or the mix-
ture of polyurethane and those components which have
already been mentioned as preferable in connection
with the description of the monocarrier granules ac-
cording to the invention is, as already indicated above,
employed as an aqeuous dispersion. Suitable diluents
in this connection in addition to water are also organic
substances, preferably low-boiling oranic solvents,
such as methanol, ethanol, butanol and 1,2-dichloro-
thane.

When carrying out the process according to the in-
vention, a process is in general employed in which
granular carrier material having a non-absorptive
surface is added to a mixer and, with continuous
mixing, sprayed with an aqueous dispersion of
polyurethane or a mixture of polyurethane and
those components which have already been men-
tioned in connection with the description of the
monocarrier granules according to the invention,
at least one liquid active compound, optionally mixed
with extenders, is then added,
optionally sprayed again with an aqueos dispersion
of polyurethane or a mixture of polyurethane and
those components which have already been men-
tioned as preferable in connection with the descrip-
tion of the monocarrier granules according to the in-
vention, and
the granular products thus obtained are dried.

The sequence in which the components are applied
to the carrier material can be varied in the manner desired
in each case.

The process according to the invention is in general
carried out at room temperature. However, it is also
possible to work at somewhat elevated temperature.

The drying temperature can be varied within a rela-
tively large range. In general, drying is carried out at
granule temperatures between 20° C. and 70° C, prefer-
bly between 30° C. and 65° C. The drying can option-
ally be carried out under reduced pressure. In addition,
the drying can either be carried out in the mixer used
for coating the carrier material or else in a separate
drying apparatus.

The process according to the invention can either be
carried out batchwise or continuously in customary
apparatus.

The monocarrier granules according to the invention
can be employed, depending on the active components
contained, for a large variety of purposes. Thus, they
can be used, for example, for combating animal pests,
fungi and/or weeds. If plant growth regulators are
contained, they can also be employed for influencing
the growth of cultivated plants.

Suitable adhesives based on polyurethane are those
systems in which the actual polyurethane compound is
formed by polyaddition of a partly esterified glycol, or
symmetrical or unsymmetrical polyglycol with an ex-
cess of isocyanate, disocyanate or polisocyanate, free
isocyanate groups being retained as prepolymers.

Polyurethanes are preferably employed which are
prepared from a saturated polyester, formed from
adipic acid and n-butandiol/n-hexanediol, by reaction
with linear iso- or diisocyanates, free isocyanate groups being retained.

Chain-lengthening and formation of an aqueous dispersion takes place owing to reaction of the prepolymer formed in this way with mixtures of water and emulsifiers.

**PREPARATION EXAMPLE**

51.37 kg of grains of quartz sand having a diameter of 0.4 to 0.8 mm are sprayed with continuous mixing at room temperature (20°C) into a mixer with 0.192 kg of an aqueous dispersion which contains 0.077 kg of polyurethane (prepared from adipic acid and n-butane-diol/n-hexanediol and reaction with isocyanate, and further reaction of the prepolymer formed in this way with mixtures of water and emulsifiers).

1.155 kg of a finely ground pulverulent mixture, which contains 0.577 kg of the insecticidal component of the formula

![Chemical Structure](image)

and 0.578 kg of highly disperse silicic acid, are then added at room temperature.

The grains of quartz sand coated with the pulverulent mixture are then sprayed with an aqueous dispersion which contains 0.22 kg of polyurethane adhesive of the above composition and a further 1.155 kg of the finely ground pulverulent mixture characterized above, which contains 0.577 kg of the active compound (I) and 0.385 kg of blue dye, are added with mixing.

The product is mixed for a further 10 minutes at room temperature and then dried in the mixer at a drying temperature of not more than 60°C.

55.0 kg of monocarrier granules having a content of 2.1% by weight of active compound of the formula (I) are obtained.

The granules are distinguished by a high resistance to abrasion.

**COMPARISON EXAMPLE**

Monocarrier granules based on polyvinyl acetate adhesive

93.4 g of grains of quartz sand having a diameter of 0.4 to 0.8 mm are sprayed with continuous mixing at room temperature into a mixer with an aqueous dispersion which contains 0.69 g of polyvinyl acetate. 2.10 g of a commercial finely ground pulverulent mixture, which contains 1.05 g of the compound of the formula (I)

![Chemical Structure](image)

are then added at room temperature.

The grains of quartz sand coated with the pulverulent mixture are then sprayed with an aqueous dispersion which contains 0.69 g of polyvinyl acetate and 2.1 g of the finely ground pulverulent mixture, which contains 1.05 g of the active compound (I) and 0.7% of blue dye are added with mixing.

The product is mixed for a further 10 minutes at room temperature and then dried in the mixer at a drying temperature of not more than 60°C.

100 g of monocarrier granules having a content of 2.1% by weight of active compound of the formula (I) are thus obtained.

The granules thus obtained exhibited heavy abrasion and softening, so that they were not suitable for practical use.

It is understood that the specification and examples are illustrative but not limitative of the present invention and that other embodiments within the spirit and scope of the invention will suggest themselves to those skilled in the art.

We claim:

1. Carrier granules having an average particle diameter from 0.1 to 3 mm and containing liquid active compounds by weight comprising approximately

   a) 50 to 99.5% of carrier granules having a non-absorptive surface,

   b) 0.1 to 20% of at least one liquid phosphoric acid derivative as active compound, and

   c) 0.1 to 4% of at least one adhesive based on polyurethane as a binder, optionally mixed with a further adhesive selected from the group consisting of polyvinyl acetate, polyvinylpyrrolidone, polyvinyl alcohol, copolymers of vinyl acetate/di-n-butyl maleate, acrylic acid ester, vinyl acetate/ethylene, vinyl acetate/ethylene/vinyl chloride, vinyl acetate/acyl acid ester, vinyl acetate/vinyl ester and styrene/acyl acid ester.

2. Carrier granules according to claim 1, wherein the active compound is a plant protection agent.

3. Carrier granules according to claim 1, wherein the active compound is a liquid phosphoric acid ester.

4. Carrier granules according to claim 1, containing as an additive at least one of an extender, dye, water and an organic solvent.

5. Carrier granules according to claim 1, containing fine-grain inorganic solids as an extender.

6. Carrier granules according to claim 1, containing an inorganic pigment as a dye.

7. Carrier granules according to claim 1, containing methanol, ethanol, butanol or methylene chloride as an organic solvent.

8. A process for the preparation of carrier granules containing liquid active compounds according to claim 1, comprising

   a) spraying into a mixer granular carrier material having a non-absorptive surface and an aqueous dispersion of a polyurethane adhesive, optionally with the addition of a thickener and optionally with an aqueous dispersion of a further adhesive selected from the group consisting of polyvinyl acetate, polyvinylpyrrolidone, polyvinyl alcohol, a copolymer of vinyl acetate/di-n-butyl maleate, acrylic acid ester, vinyl acetate/ethylene, vinyl acetate/ethylene/vinyl chloride, vinyl acetate/acyl acid ester, vinyl acetate/vinyl ester and styrene/acyl acid ester,

   b) then adding a mixture containing the liquid active compound and an extender, optionally again spraying the product with an aqueous dispersion of the further adhesive,

   c) and then drying the granules.
9. In the combating of agricultural and horticultural pests by applying to a locus from which it is desired to exclude such pests a normally liquid active compound and a normally solid active compound, the improvement which comprises applying such active compound in the form of granules according to claim 1.

10. Carrier granules according to claim 1 of an average particle diameter from 0.3 to 1 mm and by weight comprising approximately 60 to 92% of carrier granules, 0.5 to 15% of phosphoric acid derivative and 0.3 to 3% by weight of adhesive.